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Tb(III) complexes with nonyl-substituted calix[4]arenes as building blocks of hydrophilic luminescent mixed polydiacetylene-based aggregates

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ABSTRACT

The present work for the first time introduces PDA-based vesicles as convenient supporters of luminescent water insoluble Tb^{3+} complexes. The specific cyclophanic structure of the ligands, where upper and lower calix[4]arene rims are decorated by nonyl- and chelating groups correspondingly provides both complex formation with Tb^{3+} ions with the coordination of the latter *via* two 1,3-diketonate groups and self- or mixed aggregation of the complexes. The conditions of the self-aggregation of the Tb^{3+} complexes are revealed, although the self-aggregates are unstable being converted into the nanosized precipitates which tend to further aggregation and phase separation. The complexes exhibit Tb(III)-centered luminescence which tends to change in time following the phase separation processes. The embedding of the Tb^{3+} complexes into the PDA-based vesicles results in the mixed aggregates with significant Tb(III)-centered luminescence and significant colloidal stability. The latter arises from high negative electrokinetic potential values due to exterior carboxylic/carboxylate groups of the PDA vesicles.

1. Introduction

Luminescent lanthanide complexes are of growing interest as convenient platform for development of sensing procedures. In particular, lanthanide-centered luminescence plays significant role in sensing of biomolecules and drugs in aqueous solutions due to easy luminescence response on a complex formation event [1–17]. The use of lanthanide complexes in sensing poses a problem of water solubility of the sensors. Thus, tools for enhancement of lanthanide complexes water solubility are worth discussing. The use of hydrophilic ligand environment of lanthanide ion is well known way to gain in a water solubility of lanthanide complexes [2–5]. Great success in nanotechnology is the reason for development of hydrophilic core-shell nanoparticles exhibiting Tb(III)- and Eu(III)-centered luminescence which are good alternate to the water soluble complexes [6–17]. Nevertheless, both specificity of the core-shell morphology and nature of the hydrophilic shell are of great impact on sensing properties of the nanoparticles. Therefore, both developing new morphologies of hydrophilic nanoparticles with lanthanide-centered luminescence and revealing main driving forces of the self-assembly processes converting luminescent molecular blocks into hydrophilic nanoparticles are the challenging tasks from both practical and fundamental points of view.

Polydiacetylene (PDA) vesicles have gained great attention during recent decades as excellent basis for sensing procedures. The sensing and imaging procedures have been developed under modification of PDA vesicles by biomolecules, such as phospholipids, glycolipids and cholesterol [18–20], where embedding of amphiphilic biomolecules resulted from inclusion of their hydrophobic moieties into the hydrophobic layer of PDA-based vesicles modifies their binding and sensing ability. Embedding of artificial amphiphilic molecules into the PDA vesicles provides alternative route of their modification. This route is well exemplified by surfactants and amphiphilic calix[4]arenes [21,22]. The embedding of fluorophoric molecules to the PDA vesicles provides additional tool to develop novel sensing procedures [23,24], while the application of metal complexes as the fluorophores [25] is more scarce than that of organic dyes. However, a use of PDA vesicles as carriers for luminescent lanthanide complexes can be regarded as promising alternative route in development of hydrophilic nanoparticles with lanthanide-centered luminescence, although such route is very scarcely highlighted in literature.

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